REFRACTORIES IN HEATING UNITS

ANALYSIS OF THE EFFECT OF PERICLASE-CARBON REFRACTORY QUALITY ON CONVERTER LINING LIFE

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Results are provided for comparative analysis of claimed physicochemical and physicoceramic properties of periclase-carbon objects from different producer firms. Supplementary research determines the properties of periclase object charge components (periclase and carbon purity and grain size, strength before and after coking firing, and other parameters). Converter wall and bottom residual thickness are analyzed with comparison of operating conditions.

Keywords: converter, lining, periclase-carbon refractories, antioxidants, lining differentiation.

Considerable attention is currently devoted to the question of periclase-carbon refractory quality. This is connected with the fact that the amount of these refractories used is quite large in ferrous metallurgy plants. Lining life depends on their quality. With existence of reliable information about object quality, used in metallurgical plants, it is possible with greater probability to predict plant life and to select the most optimum versions for operation, and consequently a refractory material supplier. Periclase-carbon objects are used in the most critical plants of ferrous metallurgy (converters, steel-pouring ladles), and therefore OAO EVRAZ NTMK studies any proposal concerning these plants.

Existing Russian standard documents provide properties, of which the most reliable is raw material chemical composition, and consequently a refractory from which it is manufactured. The rest of the properties are derived from manufacturing parameters, equipment, both manufacturing and laboratory, existence of independent monitoring, worker qualifications, etc. Detailed information is particularly necessary for the quality of refractories used in view of an increase of introduction of innovations into cast iron and steel production, and correspondingly with toughening of refractory service conditions. Refractories for lining converters are quite expensive. The market offers for these materials are quite extensive, and therefore choice of the highest quality refractories, adapted for specific operating conditions, is very important for the economy of an enterprise.

Currently within OAO EVRAZ NTMK a program is being implemented for increasing steel production in converters up to 4.5 million tons per year against a planned 3.5 million tons. Determination of organizational and production stages for this program have been implemented previously, and this has made it possible to increase steel production, but complete solution of this task is planned primarily due to increasing converter lining life to 7000 melts or more against 4000 before adopting the program, i.e., by reducing the number of relinings. An increase in volume of production and improvement in converter lining life, are incompatible plans at first glance since in order to increase life it is necessary to determine the specific time required for lining maintenance, and this is unavoidably connected with downtime and loss of production volume.

A feature of converter production of OAO EVRAZ NTMK is smelting steel with use of a duplex process, in whose first stage devanadization of pig iron is carried out with exclusion of the slag obtained, as a commercial product, from the subsequent process. In view of this steel smelting in the second stage of the process is complicated by a small amount of slag, which it is necessary to modify not only with magnesia additions, but also to increase its amount artificially for further blowing and lining protection. Nine firms took part in implementing the plan for increasing lining life, who presented proposals for refractory material quality and

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materials for lining maintenance, and also for logistics of carrying out repairs.

All of the refractory objects proposed for converter lining were manufactured in China based on Chinese fuzed periclase, graphite, phenol resin, and antioxidants using highly efficient equipment for well-known manufacturing technology of carbon-containing refractories, whose production is based on observing the following main conditions [1, 2]:

– use of chemically pure fuzed periclase powder with a minimum iron oxide and iron impurity content;

– use of high compaction pressure for preparing a dense object structure;

– use of combined carbon-containing component, including a binder of specific chemical composition.

During tendering a study was made of quality indices and repair logistics, and choice of products from several firms, for whose testing there was careful examination.

Results of tests showed significant divergence in lining life. All of the objects analyzed were separated into three groups depending on their proposed life in a converter lining: short life (first group of objects), satisfactory life (second group of objects), and long life (third group of objects). A long lining life, i.e., not fewer than 7000 melts per campaign, satisfactory is higher than the level achieved at the time of implementing the project (5500 – 6500 melts), and short life corresponded to the level of lining life before the start of project development (4000 – 5500 melts). Additional studies were also carried for refractories of these groups. Analysis of refractory object properties with respect to groups, provided in accompanying documentation, are presented in Table 1. For conditions of confidentiality neither the name of a firm nor their affiliation to any of the products checked are provided, and also some properties that are features of the refractory manufacturing technology are not given. The main properties of objects that as a rule are present in a firm's advertising material are not a commercial secret and are provided in Table 1.

It follows from Table 1 that the properties claimed are for objects of three groups, which provide a differential approach to converter lining design for an individual area. Refractory properties for the rest of the firms differ insignificantly from each other. The binder used by almost all producers is a combined binder based on synthetic resin with addition of pitch. Addition of pitch to a binder increases high-temperature strength of periclase-carbon objects. Combined antioxidants are used in all groups of objects: aluminum metal or a mixture of aluminum with silicon, and also an aluminum alloy with magnesium, silicon and boron carbides.

Recently a tendency has appeared of excluding antioxidants from periclase-carbon object charges. There is no theoretical basis for this in publications, but practice of using these refractories (according to verbal information from specialists of several firms) has demonstrated a specific advantage of them in operation. Apparently, combined oxidizing and reducing reactions of antioxidants, occurring within a carbon object, are accompanied by gas formation and may cause weakening of its structure. From our point of view presence of an antioxidant is necessary in such areas as the upper cone where the effect of oxygen on a lining is particularly perceptible, both due to intense oxygen blowing, and also due to oxygen from the atmosphere during various stoppages of converter operation.

Introduction of antioxidants in a periclase-carbon object charge has been used extensively from the very beginning of their application, even before introduction of nitriding during slag blowing. Subsequently in view of extensive introduction

TABLE 1. Object Quality Indices Claimed in Statements

Properties	Objects with life		
	short (<5000 melts)	satisfactory (>5500 melts)	long (>7000 melts)
Raw material: periclase	Fuzed	Fuzed	Fuzed
Content, wt.%:			
MgO	96.5 – 98.0	>97	97 – 98
Graphite	8 – 16	9 – 15	9 – 17
Binder	Pitch-bonded	Resin + pitch	Carbon + pitch
Antioxidant	Al, (Al + Si + SiC), (AlMg + B4C)	(Al + Si), B4C	(Al + SiC), AlMg, Al
Number of object types in lining, differing in properties	3 – 4	5	6
Ultimate strength in compression, MPa	>40*	41 – 42*	35 – 65**
Open porosity, %	<4.0	<4.0	1.0 – 4.0
Apparent density, g/cm^3	>3.0*	2.98**	2.94 – 3.18**

* For all objects.

* For different object grades in relation to lining area.

of steel nitriding penetration of nitrogen into pores, microcracks, and lining joints, has been observed, and information has appeared about previous reaction of antioxidants with formation of nitrides, which subsequently break down under action of oxygen. However, there are no reliable data about the effect of nitrogen on operation of periclase-carbon objects containing antioxidants.

Producers explain manufacture of objects without antioxidants by the fact that aluminum powder is an explosion hazard substance, and passivated aluminum is a less active component than powder. Exclusion of antioxidants is also considered from the economic side of production, since during smelting of specials steels with an ultra-low aluminum content it is necessary to use objects not containing aluminum.

In publications for carbon refractories [3, 4] presence of aluminum in periclase-carbon objects is connected with formation of aluminum carbide, but the amount of antioxidant within the volume of an object is small (mainly <3%), and carbide formation cannot have a fundamental effect on object service properties. If aluminum carbide forms, then it is only localized. It has been established [5] that aluminum metal in a charge composition is not only an antioxidant, but it also determines occurrence of gas transport chemical reactions for formation of carbide and oxynitride phases, and this changes the structure of a refractory object during operation, increasing the proportion of pores with a radius from 0.005 to 4.5 μm. In view of this a study of the effect of antioxidant on the structure of periclase-carbon objects under conditions of continuous skull application to a lining and absence of direct action of oxygen is of separate scientific interest, since in each case introduction of a more stable oxide (Al_2O_3) into a charge increases the stability of less stable oxide (MgO), reducing Gibbs energy [6, 7]. Thermodynamic stability of oxide refractories under strictly reducing conditions has become a more important factor in recent years.

The next difference is the degree of lining differentiation, which is least for the first group of objects and greatest for the third group. Differentiation of a lining involves more uniform lining wear with respect to areas, and on the whole increases operating life. In view of this the first version of a lining is the most suitable.

Ultimate strength in compression for all group is almost identical, although in areas of increased wear the strength of objects of the third group is more than 50 MPa, which exceeds the index for objects of the first and second groups. The lowest porosity applies to objects of the third group. Analysis of periclase-carbon objects has shown that the best version for lining is refractories of the third group. In spite of some differences in properties all of them should have a life increasing smoothly from objects of the first group to the third. In fact, objects showed a life of fewer than 5000 melts to more than 7000.

In order to establish reasons for variation in lining life petrographic and thermogravimetric studies were carried out, microstructure and slag penetration of refractories were eval-

TABLE 2. Some Properties of Periclase-Carbon Object Charge Components

Properties	Objects with life		
	short (<5000 melts)	satisfactory (5500 – 6500 melts)	long (>7000 melts)
Periclase powder	Fuzed	Fuzed	Fuzed MgO + ~5.0% sintered with crystal sizes 80 – 100 μm
Fuzed periclase crystal size, μm	300 – 500 – 580 – 600 – 740 – 760 – 800 – 900 – 1500 – 1800	1500 – 2000	800 – 1000 – 1100 – 1200 – 1300 – 1500 – 1600
Grain porosity, %	3.0 – 6.0	1.5 – 2.0	3.0 – 5.0
Impurities in periclase powder	Unmelted (5 – 8 %)	None	Unmelted (<3%)
	Loose periclase grains (100 – 120 mm). Magnesium carbonate, monticellite (1.5 – 2.5%). Bicalcium silicate	<1.0 (forsterite)	<1.0 (iron oxides and silicates)
Graphite flake size, μm	(50 – 90) (150 – 250)	150 – 250	60 – 100 – 150
Amount of antioxidant, %	3.0 – 5.0	2.0 – 3.5	0.5 – 3.0
Reduction in ultimate strength in compression after coking	Factor of 1.5	Factor of 1.5	Factor of 1.3
Porosity (act.) %			
before coking	2.7	2.3	2.0
after coking	8.3	7.2	7.0
Disclosed comments	Contamination of fuzed periclase with 5 – 8% unmelted material. Some grades of object did not correspond to STD specifications	Individual grades did not correspond to STD specifications	None

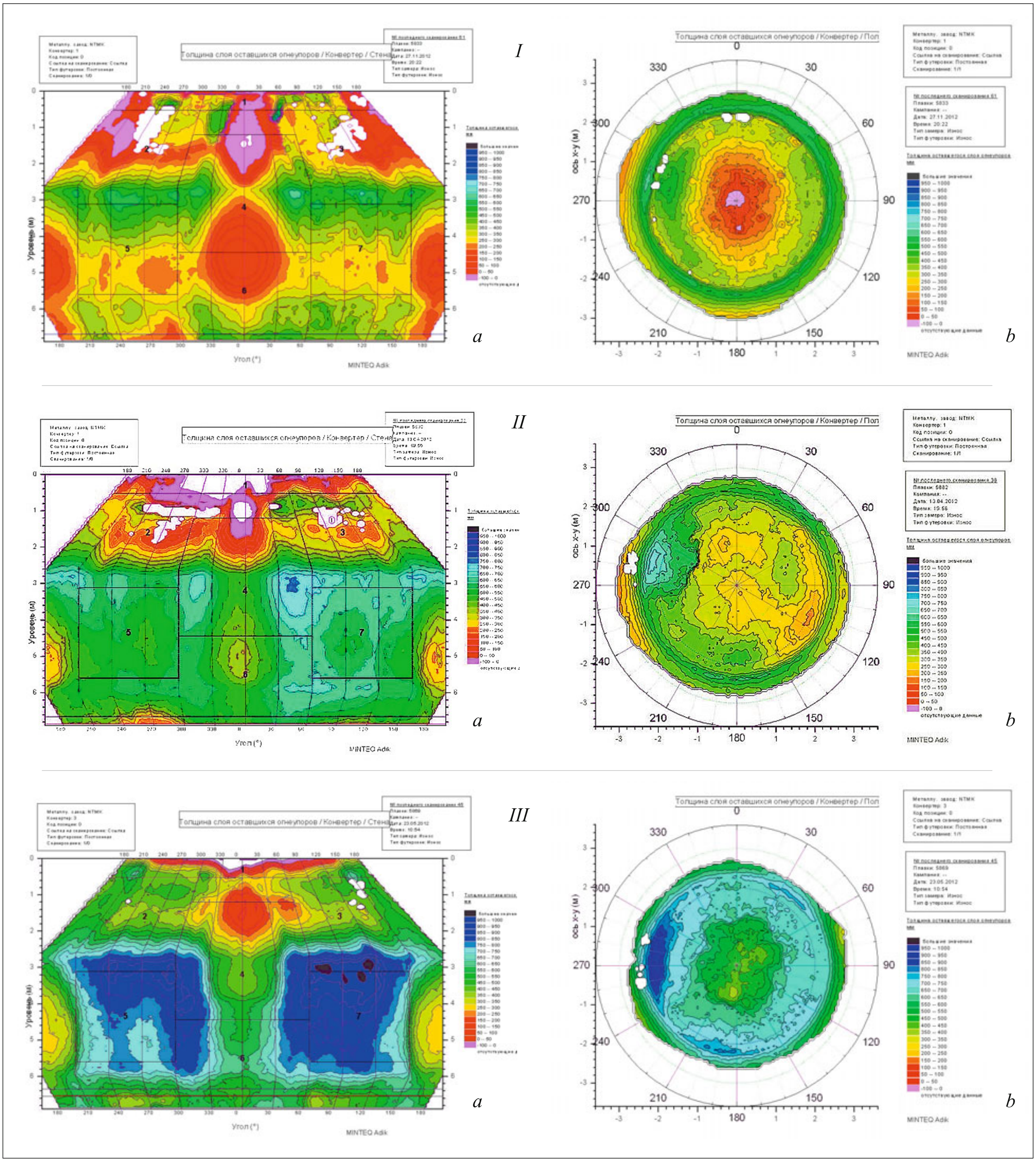

Fig. 1. Residual thickness of converter wall (*a*) and bottom (*b*), lined with objects of third (*III*), second (*II*), and first (*I*) groups.

uated, and specimen physicomechanical properties were also determined. It was confirmed that the main component of periclase refractories is fuzed periclase, whose amount was evaluated according to the following parameters: chemical composition, i.e., periclase should contain a maximum amount of MgO, and consequently minimum amount of impurity oxides; the size of crystals, porosity, and grain density.

It is well known that the greater the size of periclase crystals, it is more resistant to corrosion and erosion, has power porosity, and greater density [1]. Results are provided in Table 2.

As follows from Table 2, the main difference of periclase-carbon refractories involves the original amount of periclase powder: impurity content and greatest crystal size. Average periclase crystal size is least for objects of the first group and greatest for objects of the second group. In this case a larger crystal size appeared to be inefficient in refractory manufacture, since due to high compaction pressure cracks and defects appeared within them, through which crystal breakdown occurred, in spite of the fact that porosity appeared at a level of 1.5 – 2.0%. Within a charge of the third group of objects periclase was introduced with a different crystal size, the same as for graphite, which points to more complex manufacturing technology for objects and their differentiation in making a lining.

In manufacture of objects of the first group instead of fuzed periclase an unfuzed skin for a block was used, containing magnesium carbonate, whose presence is confirmed by derivatographic and petrographic studies. From this skin readily melting silicates are introduced into a charge composition, which reduce the final quality of periclase filler. Unfuzed periclase was also noted in a charge of periclase-carbon objects of the third group, but it was contained in a smaller amount and introduced fewer impurities into an object.

In OAO EVRAZ NTMK there is obligatory input monitoring of carbon-containing refractories with respect to physical properties before and after coking firing. This test evaluates the quality of binder used: the greater the coking residue content, the higher is refractory ultimate strength in compression after coking firing. Strength properties of objects after coking firing as a rule are worse, but to different extent for the products of different firms. In some cases it even increases, which is of greatest interest for practice (this is typical for spinel-carbon refractories). In this case the ultimate strength in compression is reduced, but porosity increases from the first to the third group of objects. These relationships clearly correlate with converter lining life.

Results of studying metal and slag resistance for specimens of objects showed that those of the first group are decarburized to a greater extent during testing, and the decarburized layer has lower strength, which is caused in all probability by a greater content fine flaky graphite within a charge with a high degree of oxidizability. Converter lining wear is shown in Fig. 1 for objects of three groups with the same lining life.

Undoubtedly operating parameters and lining quality affect lining wear, and correspondingly its life. As far as lining quality is concerned assembly of a converter lining and steel pouring ladles is carried out by qualified specialists of OAO EVRAZ NTMK under control of a firm's representative, i.e., suppliers of objects.

Concerning operating conditions it may be confirmed that as a life of 4500 melts is approached object parameters (both negative and positive) average out. In the near future materials will be prepared making it possible to evaluate the effect of both quality of work and operating conditions on converter lining life.

CONCLUSION

Quality indices have been analyzed for periclase-carbon objects manufactured by different suppliers. From the results of lining operation for objects of different suppliers they were separated into three groups with respect to the number of converter melts. In order to clarify reasons for breakdown of linings additional physicochemical and physicoceramic studies have been carried out for objects, and this has made it possible to explain the divergence in lining life and to reveal empirical relationships making it possible to predict converter lining life.

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